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Thixotropy of magnetorheological gel composites: experimental testing and modelling

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Abstract

Magnetorheological gel (MRG) is known as an aspiring controllable composite which exhibit rapid and reversible structural changes subjected to magnetic fields. Its rheological manifestation of the structural changes induced by both the shearing flow and the magnetic field is the varying in viscosity or shear stress. This effect is called thixotropy if the structural changes are reversible and time dependent. In this study, time dependent rheological properties were characterised by a proposed stepwise experiment which revealed the effects of shear rate, magnetic field, and resting time on the structural break-down and rebuilding in MRG. The results indicated up to 15% decrease in the shear stress of MRG under the constant shear rate of 6000 1/s within 5 seconds. 4 seconds and 30 seconds of resting allows approx. 50% and 98% recoveries of the reversible structural change, respectively. The application and intensifying of magnetic fields tend to increase thixotropic yield stress but decrease the fluctuation state. A simple model was formulated to capture the unique time dependent structural changes of MRG under constant shear flow and magnetic field; and, showed accurate predictions of the thixotropic responses of MRG under the magnetic fields, shear rates and resting time considered.

Keyword: Magnetorheological gel; Thixotropy; Thixotropy model; Flocculation

Highlight

1. A mini review on thixotropy.
2. Thixotropy of MRG is characterised by a stepwise testing protocol.
3. A thixotropy model is proposed for MRG.

4. Influence of thixotropy on magnetorheological material applications is discussed.

1. Introduction

Magnetorheological gels are comprised of micron-sized ferromagnetic particles, i.e., nickel particles, iron particles and carbonyl iron particle (CIP), and polymeric gel matrix, i.e., polyurethane and carrageenan [1-3]. The free-flowing ferromagnetic particles dispersed in the gel matrix can form chain-like and columnar microstructures that aligned with the flux direction of the applied magnetic field. By adjusting the density of the applied magnetic flux, the tannable material properties can be achieved, so-called magnetorheological (MR) effect. Among MR materials, MRG can be placed in the intermediate between MR elastomers [4-6] and MR fluids [7] and mitigates their inherent limitations. In MR elastomers, the elastomeric matrix trapped the mobility of ferroparticles, thus resulting in approx. 50 times lower MR effect than that of MRG which can exhibit over 200 times increase in the storage modulus [8, 9]. Owing to the higher viscosity of polymeric matrix than the carrier oil of MR fluid, MRG showed significant enhancements in the shear stress, sedimentation performance and application stability compared with MR fluids [10].

Despite the fact that using polymer as matrix offers fascinating improvements for MR materials, compositions of high viscosity polymer and particles normally exhibit reversible and irreversible structural changes which highly depends on the shear flow rate and the recent history of flow [11]. The time-dependent reversible change under flow is defined as thixotropy [11]. This phenomenon is reflected to the microstructures in the suspensions, i.e., junctions of polymers and particle flocs, which take finite time to evolve to another state and back again when subjected to different flow conditions and resting. During the thixotropic transition, three kinds of interactions were normally identified: structure break-down by flow stress, build-up by collisions in the flow and Brownian motion. Due to Brownian motion, molecules are constantly agitated and the elements in the suspension will move to positions or state where sufficient attractive force can be provided to form these elements into microstructures. The thixotropic behaviour in the particle filled polymer suspensions is thus inevitable.

At the macroscopic level, after the steady state of the composite is reached, the correlation of yield stress and shear rate can be well portrayed by rheological models, i.e., Bingham, power law and Hershel Bulkley models. But the shear stress evolution over time between successive steady flows of different shear rates cannot be properly described by the yield stress models. In Fig. 1, the red dashed lines refer to the resulted shear stress in respect of the transitions of shear rates (the black solid line) over time. As the linear increased shear rate is applied to a material which has been rested for t_1 seconds, the shear stress grows linearly to the static shear stress noted as τ_{0s}. After t_2 seconds, τ_{0s} gradually decreases to a dynamic yield stress τ_{0d} under a constant shear rate as the balanced state of flocculation and de-flocculation processes was reached. As the instantaneous increase and decrease of shear rate occurred at t_3 and t_4, the delayed response of shear stress is caused by the thixotropy in the composite. It has been shown recently in several investigations that τ_{0s} and the delayed response of shear stress is associated with resting time and shear rate; and τ_{0d} does not relate to the past flow history [12, 13].

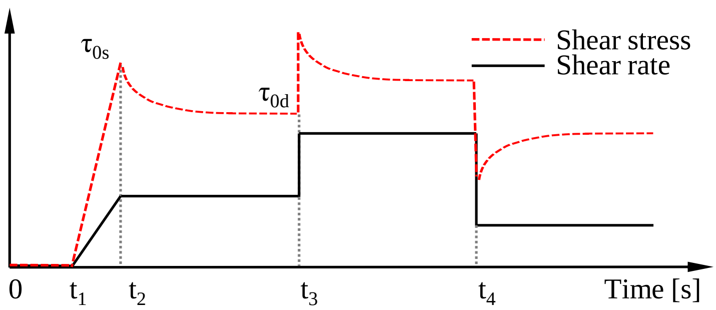


Fig. 1. Shear stress evolution under changing flows.

However, thixotropy in magnetorheological suspensions is complicated by the involvement of magnetic fields which not only vary the steady states τ_{0d} values, but also constantly interfere the flocculation and de-flocculation of the ferroparticle microstructures. In the recent investigation by Wang *et al.* [14], cellulose nanocrystal filled MR fluids were fabricated and exhibited 7000-fold increase in the shear stress as the magnetic flux density increased from 0 to 0.3T. The thixotropy loop induced 3000 time increase in the enclosed loop area which refers to the magnitude thixotropic behaviour. Li *et al*. reported the similar finding that magnetic fields tend to increase the enclosed areas of thixotropic loop [15]. Stepwise experiments were also performed and showed that the recovery of ferroparticle microstructure is rather quickly under the magnetic field. Although characterising time-dependent rheological behaviour by thixotropy loops has limitations, which will be detailed in *section 2.4*, the current findings suggested that magnetic field acts differently on the rheological behaviours and the evolutions of microstructure in the MR fluids.

For polymeric-gel-based MRG, the influence of magnetic field on the thixotropy has not been investigated before. As a promising candidate to improve the stability, sedimentation performance and control precision of shear mode controllable devices, i.e., dampers, suspensions, and clutches , the ignorance of thixotropic effects may result in the degradation of control precision during the starting state and transitions between two stead states of the developed applications. Thus, the characterisation of the time dependent rheological effects for MRG is of urgent demand.

In this paper, a mini review is prepared to elaborate the physical explanation, characterisation, and modelling of thixotropy first. Then the proposed methods for characterising and modelling the thixotropy of MRG with considering different resting time, shear rate and magnetic field will be presented. Predictions from the proposed model will be validated with the experimental results from the rheometer. Finally, discussions on the thixotropy of MRG from the engineering application perspective will be presented.

2. Literature review

2.1 Physical explanations of thixotropic behaviour under magnetic fields

One of the classic explanations of thixotropy is presented in [16]. Interactions between particles and carrying matrix decide the potential energy well, noted as ΔE, for a particle. As shown in

Fig. 2 (a), the particle will be trapped in the well unless an energy higher than the ΔE was given to the particle by the external stress or strain. In the macroscopic view, flow occurs after certain number of particles leave their potential energy well, which is call yield stress behaviour. For a thixotropic system, the ΔE increases when the resting time prolongs, as the result of the interaction of Brownian motion and evolution of the dispersion microstructure during resting.

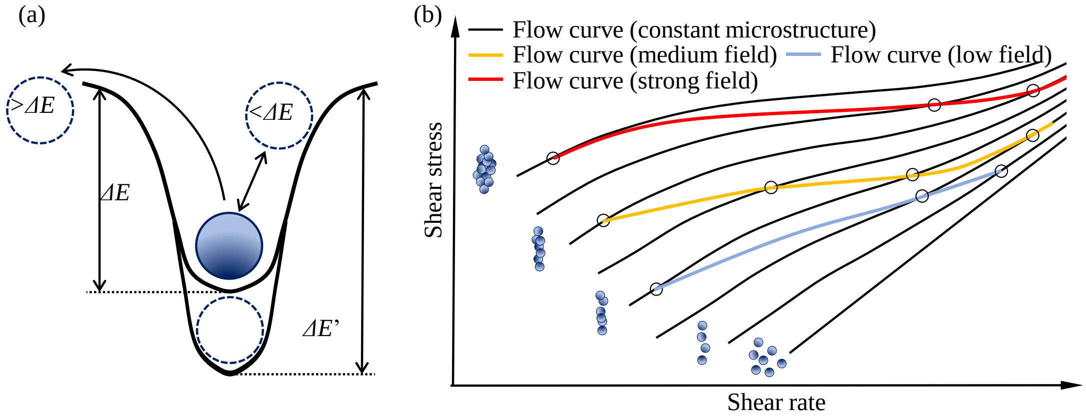


Fig. 2. (a) Physical explanation of thixotropy for particle filled dispersion without magnetic field. (b) Microstructure and flow curves.

For a thixotropic system containing ferroparticles under magnetic fields, this theory becomes inadequate to quantitively explain the energy required for a particle to leave the well at the microscopic level, due to localized anisotropy caused by the formation ferroparticle chain structures. Particles in or near the chain structure require much higher energy to leave the well than that of a free-flowing particle. Also, the size of the chain structure affects the energy required for a particle to leave the structure as larger chains have lower magnetic reluctances that gives higher flux densities and attracting forces on particles. As a result, the thixotropic behaviour in ferroparticle suspensions could be explained from the macroscopic level when flow occurs.

To illustrate the influence of magnetic field on the particle interactions and flow behaviour, Fig. 2(b) was prepared. In Fig. 2(b), black lines indicate the flow curves for different degrees of flocculation and can be treated as imitations for the flow curves for different sizes of the ferroparticle chain structures under varying magnetic field with assumption that the flocculation will not break-down when subjected to increasing shear rates. In reality, the sizes of the flocculation are not constant because break down and rebuild of the microstructure take place constantly. As the magnetic field involves, the attractions between particles become stronger and the evolutions between degrees of flocculation become dependent on the field. On Fig. 2(b), the equilibrium curves intersect with lower flow curves for the decreased flocculation sizes as the shear rate increase; and the involvement of magnetic field results in different initial flocculation status and decreasing pattern of flocculation size throughout the shear process. When a balance state between the de-flocculation and flocculation of the particles is reached, the equilibrium curve will follow the flow curve of a particular size.

2.2 Thixotropy models

Towards the modelling of thixotropic effect, two major techniques were reported: phenomenological models and micromechanical models [17, 18]. Micromechanical models focus a scientific interpretation in terms of the material compositions, mechanisms, and physics laws. On the contrary, phenomenological models aim to provide general description of the mechanical behaviour of material under complicated characterisation conditions. However, no definitive model is available for both approaches due to complicated nature of thixotropy and the wide range of thixotropy materials. In this review, only phenomenological models will be discussed as they are more versatile and easier to be introduced to the MR materials compared with micromechanical models.

For a phenomenological model of rheological behaviors, viscosity is one of the fundamental parameters to be described, i.e., $\eta = \tau/\dot{\gamma}$ where τ is the shear stress and $\dot{\gamma}$ is the shear rate. To portray the time dependent microstructure, flocculation parameter λ is introduced as a function of time. This parameter represents the instantaneous status of structure or the “degree of jamming” [19]. In literatures, structure evolution equation for λ is assumed to be dependent on the instantaneous flow condition $\Pi_{\dot{\gamma}}$ and the instantaneous structure [20]. Thus, the thixotropic behavior can be represented as:

$$\begin{aligned} \tau(t) &= f_1\left[\lambda(t), \Pi_{\dot{\gamma}}(t)\right] \\ \frac{d\lambda(t)}{dt} &= f\left[\lambda(t), \Pi_{\dot{\gamma}}(t)\right] \end{aligned} \tag{1}$$

Coussot *et al*. [21] adopted the similar principle and proposed the expression of λ to represent the thixotropy:

$$\begin{aligned} \eta &= \eta_0(1+\lambda^n) \\ \frac{d\lambda(t)}{dt} &= \frac{1}{\theta} - \alpha\dot{\gamma}\lambda \end{aligned} \tag{2}$$

where η_0, n, θ and α are material parameters. This model has been proven to be effective for Bentonite suspensions though validate with the magnetic resonance imaging and simulation [22]. Based on this advancement, this model has been adopted to model the thixotropy for cement paste [12]. Roussel [23] derived Eq. 2 to the following form:

$$\begin{aligned} \tau &= (1+\lambda)\tau_0 + k\dot{\gamma}^n \\ \frac{d\lambda}{dt} &= \frac{1}{T\lambda^m} - \alpha\dot{\gamma}\lambda \end{aligned} \tag{3}$$

Where T, m and α are thixotropy parameters and the flocculation state λ is dependent on the flow history. For a state where the steady shear stress is reached, the λ becomes zero which means the thixotropy apparent yield stress $\lambda\tau_0$ is fully eliminated under a constant shear flow. λ will evolve to larger values after resting of the materials. In equivalent to this structure evolution equation for parameter λ, fading memory integrals were applied by Wallevik *et al.* [24] to provide a more practical interpretation of the flocculation and dispersion of the grains. For the MR materials, the current practices are limited to fit the characterized rheological behavior to models that contains the structure evolution equation. Li *et al.* [15] applied the structure kinetics model to fit the recover behaviour (storage moduli G gradually increase under constant shear rate) of a ferrofluid during a low shear rate interval after a higher rate interval. The structure kinetics model can be written as:

$$\frac{d\lambda}{dt} = h_1(1-\lambda)^a - h_2\dot{\gamma}^b\lambda^c + h_3\dot{\gamma}^d(1-\lambda)^e \quad (4)$$

on the right-hand side of Eq. 4, the first to the third term are for the rate of formation of the flocculation, flow-induced micro structural break-down and the formation of the structure by shear motion, respectively. h_1, h_3, and h_3, are model constants and parameters *a* to *e* are model fitting parameters. For the recovery stage, only the first term was considered. However, the results are limited in fitting the recovery of storage moduli of the ferrofluid under one magnetic field level.

2.3 Characterisation methods of thixotropy

The rheological features exhibited from a thixotropy systems can be summarised as time dependent viscosity decrease under flow in conjunction with reversibility when the flow is decreased or paused. Based on these features, several measurement techniques such as hysteresis and step test were proposed to quantitively characterise thixotropy in various materials. However, reversible and irreversible microstructure changes, time effect and shear history all can introduce fault and limitations to the measurements. The following sections will present discussions on the measurements based on hysteresis and stepwise tests and justifications of applying these methods to characterise thixotropy in MRG.

2.3.1 Thixotropic loop

Characterising thixotropy using hysteresis loops was firstly reported by Green *et al* [25]. It plots the shear stress responses following the sequence of increasing sweep of shear rate from zero to the maximum and then decreasing sweep from the maximum to zero. If the sample is thixotropic, the measured result will show a hysteresis loop with the increasing sweep exhibiting higher shear stress values than the decreasing curve. This difference is caused by the transient nature of thixotropy. To be specific, the break down and recover of microstructures happen slower (shearing time is enough to reach steady state) than the increasing and decreasing of shear rates to the next value, respectively. The area enclosed by the two curves is used as a characteristic for thixotropy.

However, the measurement is heavily affected by the test procedure. The major concern on this test is that the test time and shear rate change simultaneously. The shear history of each measurement point thus differs from all other points. Also, number of measurement points, shear rate change between points and measurement time of each point will result in variance of loop shape. For the same increasing and decreasing shear rate range, longer measurement time and more points lead to smaller loop area. And there has no imperial guideline proposed on the setting these variables for the tests.

Moreover, the measured hysteresis area is not a physical rheological parameter. The possibility of investigating the influence of the shear rate on the microstructure evaluation over time is limited. For example, hysteresis presented in [14, 15] for MR fluids can only indicate the influence of the magnetic field on the shape and area of the loops; and larger filed density exhibits a larger loop area. The results are limited to be a qualitative identification for thixotropy and a comparison of thixotropy for MR fluids with different compositions, rather than uncover the relationships between the material resting time, shearing time, shear rate and microstructure evolutions for MR suspensions under magnetic fields.

2.3.2 Stepwise tests

To mitigate the coupling issue of time and shear rate for the hysteresis loop, methods based on stepwise changes of shear rate or shear stress were proposed. Applying the constant shear flow to a rested sample triggers a overshoot stress that will gradually decay to the steady state stress value. The steady state can be repetitively produced and treated as a reliable test reference status. This status is normally followed by intentions applications of a higher or lower value of shear rate or shear stress. As the condition of the sample before shearing is generally associated with the shear history, the influence of resting period, previous shearing and sample loading can be compared by the stepwise tests [11]. This method also provides the possibility for checking the reversibility of the experimental data by bring the shear rate or shear stress back to the initial level [15].

The stepwise experiments can also characterise another important aspect of thixotropy: flocculation process [23]. By alternatively applying the constant shear flow and zero shear rate resting interval, the flocculation status after different resting can be reflected by the response at the beginning of each shear flow. However, this aspect is normally missing in investigations of MR suspensions. In MR suspensions based adaptive devices, the shutting down or pausing of the shear motion input of the device can be considered as resting the MR suspensions in the device. Different resting time results in different static yield stress of MR suspensions, as the flocculation process constantly occurs during resting. The change of static yield stress in associate with different resting time normally cause the stress overshoot, latency of control and overfeed of magnetic field.

3. A thixotropy model for magnetorheological gels

In the case of model suitable to predict the thixotropy of MRG and potential application point of view, features other than scientific exactitude should be addressed and are listed as follow:

- the evolution between the static yield stress and dynamic yield stress over time of the MRG under different levels of magnetic field should be described by the model;
- effect of resting time under different magnetic fields should be included in the model as a reflection on the initial flocculation state λ;
- the model should be easy to apply and have least amount of parameters.

The thixotropy model for MRG is developed based on the basic thixotropy principal Eq. 3. As Bingham model is proven to be effective to describe the rheological behaviour for MRG [26], Eq. 3 can thus be written as Eq. 5 with n set to 1, K replaced by plastic viscosity μ_p and m assumed to be 0 for the scenario where the yield stress at rest increase linearly with time.

$$\tau = (1 + \lambda)\tau_0 + \mu_p\dot{\gamma} \quad (5)$$

$$\frac{d\lambda}{dt} = \frac{1}{T} - \alpha\dot{\gamma}\lambda \quad (6)$$

In the case of constant shear rate, the assumption that the characteristic time of flocculation is longer than that of de-flocculation process, the first term in Eq. 6 can be thus neglected. After integration, Eq. 6 yields:

$$\lambda = \lambda_{\text{initial}} e^{-\alpha\dot{\gamma}t} \quad (7)$$

where α is the fitting parameter. When the time t is equal to zero, the λ yields the initial flocculation state λ_{initial} of the MRG after resting. However, for the practical measurement, the shear stress response can only be recorded after the shear occurred which makes the λ_{initial} at t = 0 s point hard to be captured by the rheometer. t_0 and λ_0 were introduced to represent the time consumed to characterise the first data point and its corresponding fluctuation state at t_0. As the magnetic field may introduce variation of shear stress evolution pattern, the constant e is replaced by β for a more accurate and flexible fitting outcome of the phenomenological model. The Bingham model assumes the dynamic shear stress to be linear with shear rate. For a shear rate where the Bingham model cannot precisely output the steady state shear stress τ_0, the accuracy of the thixotropy model will be greatly degraded. This is because of the thixotropy in MRG normally shows a smaller magnitude of shear stress evolution when compared with the two or even three times change observed in concrete. A term τ_m is added to the model to compensate the inaccuracy of Bingham model. τ_m can be calculated through:

$$\tau_m = measured\ steady\ state\ shear\ stress - (\tau_0 + \mu_p\dot{\gamma}) \quad (8)$$

This term can also contribute to capture the shear stress increase caused by the remanence in CIPs which will be detailed in *section 4.4*. The developed thixotropy model for MRG thus writes:

$$\tau = \left(1 + \lambda_0 \beta^{-\alpha\dot{\gamma}(t-\mathrm{t}_0)}\right)(\tau_0 + \tau_m) + \mu_\mathrm{p}\dot{\gamma} \quad (9)$$

The flocculation state λ_0 and thixotropic yield stress $\Delta\tau$ at t_0 can thus be derived and represented as Eq. 10 and Eq. 11.

$$\lambda_0 = \frac{shear\ stress\ at\ \mathrm{t}_0 - measured\ steady\ state\ shear\ stress}{\tau_0 + \tau_m} \quad (10)$$

$$\Delta\tau = \ shear\ stress\ at\ \mathrm{t}_0 - measured\ steady\ state\ shear\ stress \quad (11)$$

4. Experimental results

4.1 Material and testing setup

The MRG sample with 60% weight fraction of CIP (spherical, 3.5 μ diameter, Beijing Xing Rong Yuan Technology Co., Ltd., China) was studied. The gel matrix is polyurethane (type CT001, Shanghai Shengju Co., Ltd., China). The polyurethane is synthesized by toluene diisocyanate and polypropylene glycol; and higher diisocyanate concentration gives higher viscosity[9, 27]. The polyurethane appears as soft gel state and has an amber hue before mixing. The fabrication process of MRG includes four steps: weighting the polyurethane and CIP following the weight ratio of 2:3; mixing the two components evenly at 60 ˚C for 30 minutes with the mixer set at 500 rpm; placing the mixture in the vacuum drying machine at the temperature of 25˚C for 2 hours to remove air bubble; resting the mixture at 25˚C for two days. The fabricated MRG is as black viscous gel as shown in Fig. 3(a). When magnetic field applied, the sample appears as semi solid with small column structures as shown in Fig. 3(b).

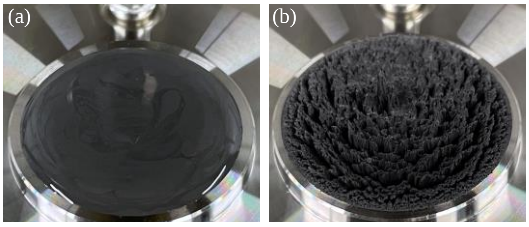
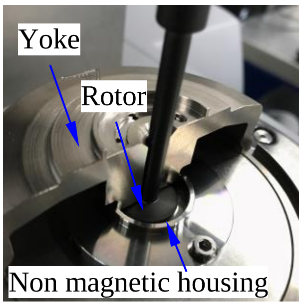


Fig. 3. (a) MRG sample. (b) MRG under magnetic field.

The rheometer used in this work is MCR 302 rheometer (Physica MCR 302, Anton Paar Co., Austria) equipped with the twin gap measurement system as presented in Fig. 4(a). The schematic of the tween gap system is shown in Fig. 4(b). In this measurement geometry, the magnetic field (red arrow line) is produced by application of direct current to the coil which is embedded under the nonmagnetic housing. The direct current is supplied by a separate power unit (PS-MDR/5A, Anton Paar Co., Austria) and controlled by the rheometer software. The nonmagnetic housing serves as the container for the MRG sample while having a slot opened at the bottom to accommodate a hall probe for the magnetic field measurement. A magnetisable disk is embedded under the nonmagnetic housing and guides the magnetic flux to the inner cylinder (20 mm diameter) where contains the MRG sample. The two-part yoke is applied as a magnetic bridge to form uniform magnetic field oriented vertically to the measurement gaps. The rotor (TG16, Anton Paar Co., Austria) is magnetisable; and the plate of the rotor (16 mm diameter; 1mm thickness) forms two 0.3 mm measurement gaps with the nonmagnetic housing and the yoke. This enclosed geometry offers the possibility of testing over 10^4 1/s shear rate and prevent the sample from centrifuging out of the housing. The deformation of MRG under magnetic field causes an increased normal force. The two gaps balance the normal forces on top and bottom of the rotor plate thus improve the measurement stability. It should be noted that the rotor measutres the total shear stress distributed on up and botton of the rotor surface and rotor rim.

(a)



(b)

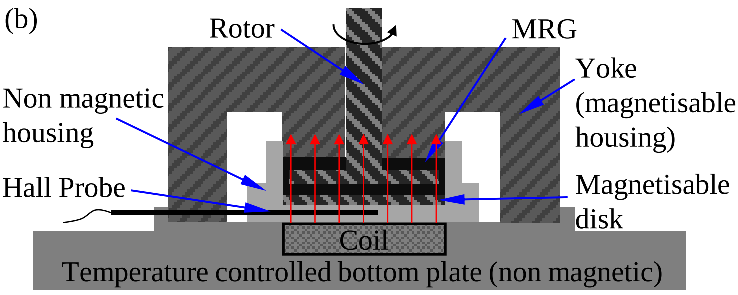


Fig. 4. (a) Photo of twin gap geometry. (b) Schematic of twin gap geometry.

Steady shear test and stepwise thixotropy test were designed to portray the time dependent rheological behaviours of MRG which will be detailed in the following sections. For all tests, four levels of current applied to the coil are 0, 0.2, 0.4, 0.6 A which can generate 0, 0.1, 0.2, 0.3 T flux density, respectively. The magnetic fields were measured by a teslameter (FH54, Magnetic Physics Inc., Germany) with a hall probe (HS-TGB5, Magnetic Physics Inc., Germany). Due to the application of current may cause the temperature increase during long timespan tests, a circulating temperature module (C-PTD 200, Anton Paar Co., Austria) connected to the bottom plate to maintain the test temperature at 21˚C ± 0.05 ˚C for all measurements. The volume of MRG loaded in the nonmagnetic housing for each test is 0.4 mL. Demagnetisation was performed immediately after every test to eliminate the remanence in the magnetisable rotor.

4.2 Steady state behaviour

The steady shear tests were firstly conducted to characterise the basic rheological behaviours of MRG at their steady states under the four levels of magnetic field. Successive shear rate steps of 3000, 4000, 5000, and 6000 s^{-1} were considered. In this experiment, each step takes 30 s when the flocculation parameter λ decreases to zero in Eq. 9. The measured results (solid lines) are fitted with Bingham model (dotted lines) as presented in Fig. 5. The expropriated values of yield stress τ_0 and plastic viscosity μ_p under the four magnetic fields are summarised in Table 1 and show the decreasing trend for plastic viscosity and increasing yield stress as the increasing of magnetic Field.

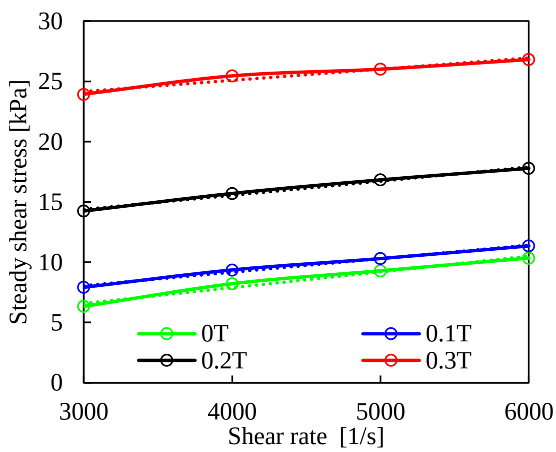


Fig. 5. Steady shear stress of MRG.

Table 1 Fitted yield stress and plastic viscosity values of MRG

Flux density [T]	0	0.1	0.2	0.3
Yield stress [kPa]	2.942	4.807	10.204	21.624
Plastic viscosity [Pa·s]	1.2312	1.102	0.98	0.8526

4.3 *Stepwise thixotropy tests of MRG*

As the thixotropy is a time-dependent and reversible behaviour, a reference state in MR gel should be carefully chosen to compare the influences of the resting time, shearing time, shear rate and magnetic field. Theoretically, the completely flocculated and de-flocculated states can be treated as candidates for referencing the influences on rebuilt and break down of microstructures. In fact, none of the two states can be reached. For the completely flocculated state, MR gel contentiously flocculates under magnetic field and the irreversible structural changes occurs, i.e., hard cake and remanence of the aggregated ferroparticles. As for the completely de-flocculated state, infinity shear rate is required.

Thus, to characterise time-dependent rheological behaviour of MR gel, an equilibrium state under a constant shear rate and magnetic field is the most suitable since the balance between the structural break down and rebuilt is reached. If the equilibrium state of a constant shear rate follows a resting time, the de-flocculation process stops and the microstructure stars to rebuild. By varying the length of the resting time, different levels of recovery can be then characterised applying an instantaneous shear motion of the same shear rate. Under different combinations of shear rates and magnetic fields, although the resulted dynamic yield stresses are different, the effect of different resting periods can be compared, as long as the shear motion and the magnetic field is constantly applied until MR gel reaches the steady state.

The proposed method to measuring method for MRG is based on the stepwise experiment. The test waveform (Fig. 6) comprises of three types of intervals which are pre-shearing interval (black sold line), resting intervals (red sold line) and shearing intervals (blue sold line), with total running time of 315 seconds. The value of shear rate is not specified on Fig. 6 as in each test only one of the four designated shear rates (3000, 4000, 5000 and 6000 s^{-1}) is configured. A 30-second pre-shearing was performed at the beginning of each test. It should be noted that, compared with other rheological characterisations, the purpose of the pre-shearing adopted in this work is to bring the MRG to the "most deflocculated" reference state (see *section 2.2*), rather than eliminating the discrepancy in the initial microstructure of the measured samples and avoiding transient behaviour. The first resting interval lasts 1 s and is placed after the pre-shearing. Then, the first shearing interval is applied for 30 s at a designated shear rate to characterise the shear stress evolution between the initial flocculation state and the steady state. Then, the resting intervals (1, 4, 10, 30 and 90 s) and shearing intervals take place alternatively. In this way, the fluctuation state at the beginning of each resting interval (or at the end of each pre-shearing and shearing interval) are the same and the influence of resting time on the flocculation process can be compared. For each shearing interval, the measuring time of one data point is 1 s thus total 30 points were sampled for each shearing interval. The magnetic is maintained at the same level throughout all intervals and four levels of flux density were considered which are 0, 0.1, 0.2, and 0.3T. New MRG sample is applied for each test and demagnetisation were performed for the measuring tool by rheometer at the end of each test.

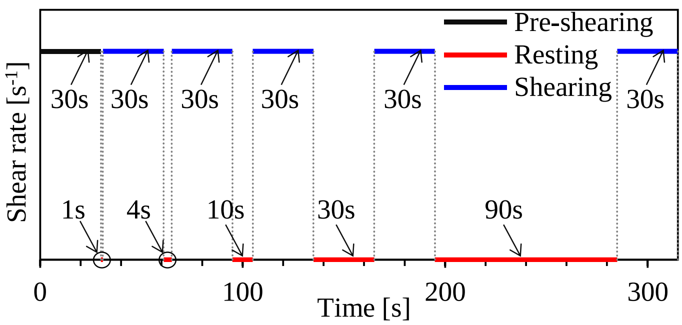


Fig. 6. Excitation waveform of stepwise thixotropy tests

The measured shear stress responses of shearing intervals are plotted as dots on Fig. 7. Fig. 7(a), (b), and (c) presents the influences of shear rate, magnetic field, and resting time, respectively. It should be noted that the time on horizontal axis is in respect to the start of each shearing interval. In this way, the flocculation state after different resting time, which is manifested by the measured shear stress at t_0 = 1 s, can be compared in a clear manner. It can be observed that, after each resting interval, the shear stress presents a decreasing trend and comes to the dynamic yield stress at approx. 10 s. And this de-flocculation process is in line with the theoretical interpretation in Fig. 1. This confirms that the rheometer is able to probe the reversible thixotropy behaviour and break the recovery during the resting interval. Under the scenarios with and without magnetic fields, the de-flocculation patterns are similar.

However, comparing the dynamic yield stress after 1 and 90 seconds resting, discrepancies can still be observed which appears to have a larger value after the 90-second resting. As shown in Fig. 7(c), the dynamic yield stress values are gradually escalated for longer resting time. These phenomena could be resulted by the irreversible microstructure change in MRG after long resting time under magnetic fields. Although CIPs are soft magnetic material which does not show magnetism when the external field is removed, the iron particles may have remanence during the long-time application of large magnetic field. The CIPs with remanence may cause a locally larger magnetic field than the external field and form larger flocs; thus, lead to larger dynamic yield stress values.

The modelling results of the proposed model are also presented as solid lines on Fig. 7 and the corresponding fitting parameters are summarised in Table 2. Firstly, the λ_0 were decided through substituting the measured shear stress at t_0 to Eq. 10. The shear stress evolution of the shearing period after t_0 can then be obtained by finding the optimal fitting parameters α and β that yield the least error between the experimaltal data and the estimation from Eq. 9. The proposed model well agrees with the experimental data.

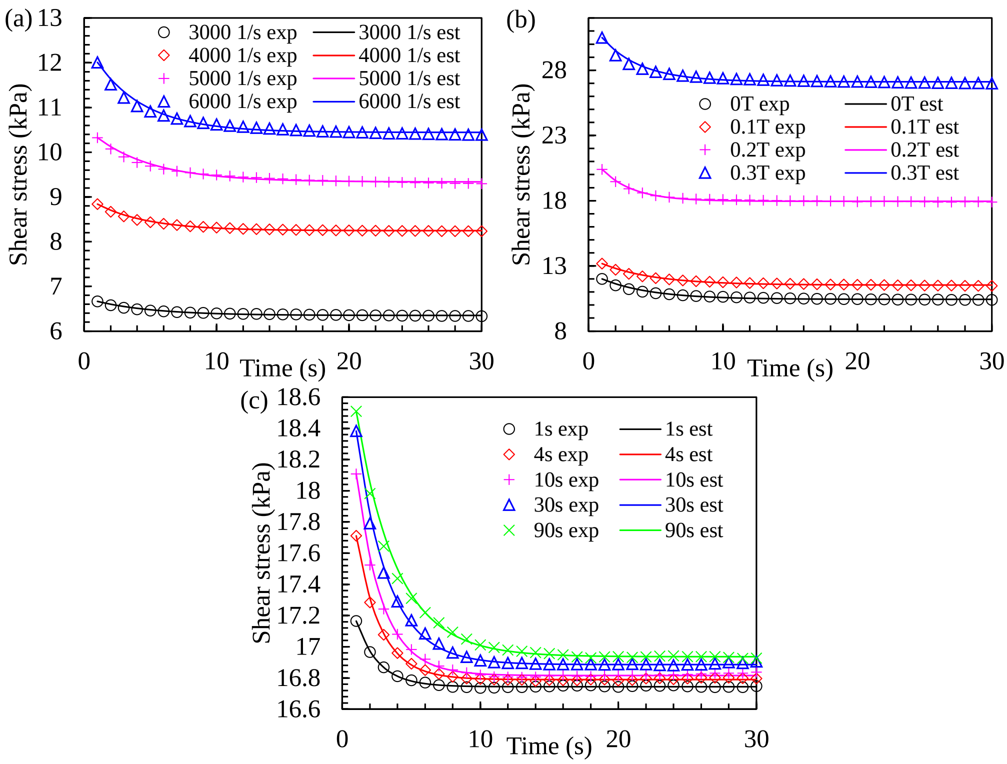


Fig. 7. Measured and predicted shear stress under (a) 0 T and 90 s resting time. (b) 6000 1/s shear rate and 90 s resting time. (c) 5000 1/s shear rate and 0.2 T.

Table 2 Summary of fitting parameter

	τ_m	α	β	λ_0
3000 1/s; 0T; 90s	-0.285	1.997E-04	1.457	0.119
4000 1/s; 0T; 90s	0.379	3.801E-05	5.532	0.180
5000 1/s; 0T; 90s	0.237	1.368E-04	1.389	0.311
6000 1/s; 0T; 90s	0.112	1.379E-04	1.387	0.514
6000 1/s; 0.1T; 90s	0.191	2.892E-05	4.309	0.330
6000 1/s; 0.2T; 90s	1.036	3.962E-05	6.092	0.218
6000 1/s; 0.3T; 90s	0.319	3.468E-05	5.328	0.154
5000 1/s; 0.2T; 1s	0.950	8.703E-05	4.085	0.038
5000 1/s; 0.2T; 4s	0.997	9.139E-05	3.483	0.082
5000 1/s; 0.2T; 10s	1.023	8.832E-05	3.322	0.115
5000 1/s; 0.2T; 30s	1.093	6.868E-05	3.568	0.132
5000 1/s; 0.2T; 90s	1.143	5.337E-05	3.618	0.139

4.4 Thixotropic yield stress and flocculation state of MR gel

To further understand the influences of magnetic field and resting and shear rate on the thixotropy of MR gel, thixotropic yield stress $\Delta\tau$ and the flocculation state at λ_0 should be discussed. As described in Section 3, thixotropic yield stress can be represented by the magnitude of stress drop between the first static yield stress and dynamic yield stress, and flocculation states refers to the "degree of jamming" and can be calculated through Eq.10. Flocculation state would decrease whenthe material is subjected to a constant shear motion and will recover after certain. Due to the first measurement point is taken at t_0=1 s by rheometer, $\Delta\tau$ and λ_0 at t_0 of MR gel is investigated.

Fig. 8(a) to (d) show the thixotropic yield stress of MR gel under the shear rates of 3000, 4000, 5000 and 6000, respectively. It can be observed that resting increases the thixotropic yield stress for MR gel as expected and is mostly effective in the first 10 seconds. After 30-second rest, the increase in the thixotropic yield stress becomes insignificant. With the increase of shear rate from 3000 to 6000 s^{-1}, $\Delta\tau$ after 90 s resting at zero field dramatically grows from 0.122 to 0.588 kPa. The increase of $\Delta\tau$ at 0.1 T is rather small compared with the zero-field scenarios. Whereas, as the fields increase to 0.3 T, $\Delta\tau$ values are two to three times higher than the zero-field scenarios under all shear rates.

λ_0 values are also plotted in Fig. 9. Compared with $\Delta\tau$, shear rate and resting time have similar effects, but magnetic field tends to decrease the flocculation states. The decreased λ_0 values stands the reduces the digree of jamming of the MRG sample as the the microstructure are orderly alined and reinforced by the increase of magnetic field. This can also be explained as magnetic field has a more apparent contribution on MR effect than on thixotropic effect for MR gel. To be specific, the 0.3 T magnetic field contributes to the increase the thixotropic yield stress compared with that of zero field. As the magnetic field has a more significant effect in raising the steady shear stress values, λ_0 tends to reduce with the increase of the field. Thus, the effect of magnetic field on thixotropy of MR gel cannot be simply concluded as an increase or decrease trend and should be carefully evaluated by both thixotropic yield stress and flocculation status.

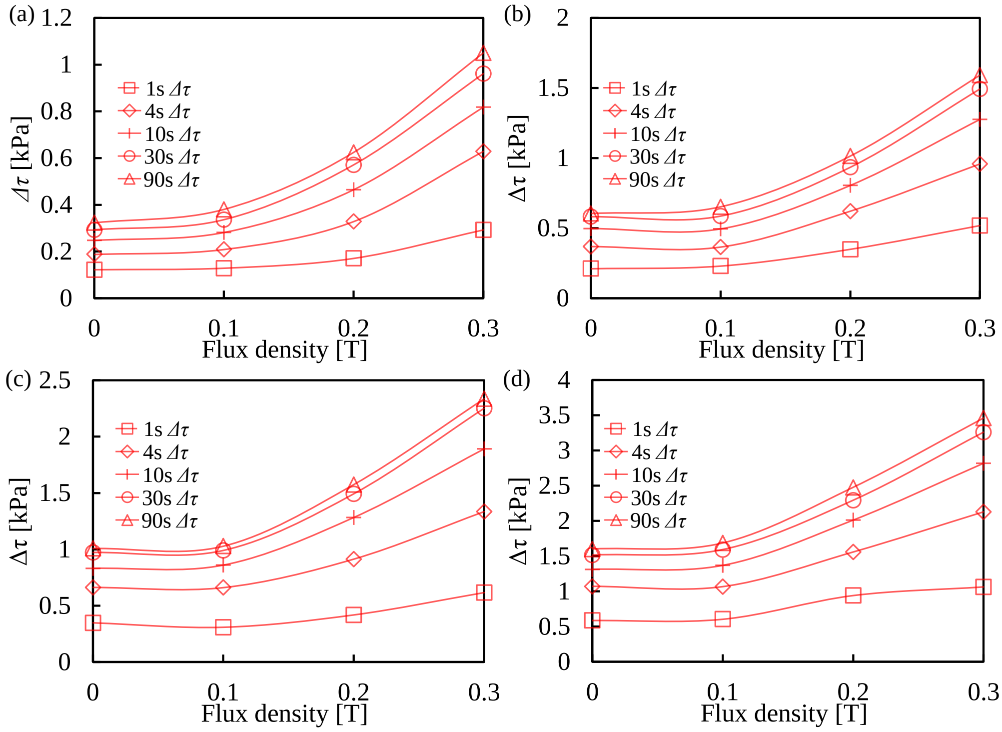


Fig. 8. Influence of magnetic field and resting time on thixotropic yield stress of MR gel under shear rates of (a) 3000 s^{-1}. (b) 4000 s^{-1}. (c) 5000 s^{-1}. (d) 6000 s^{-1}.

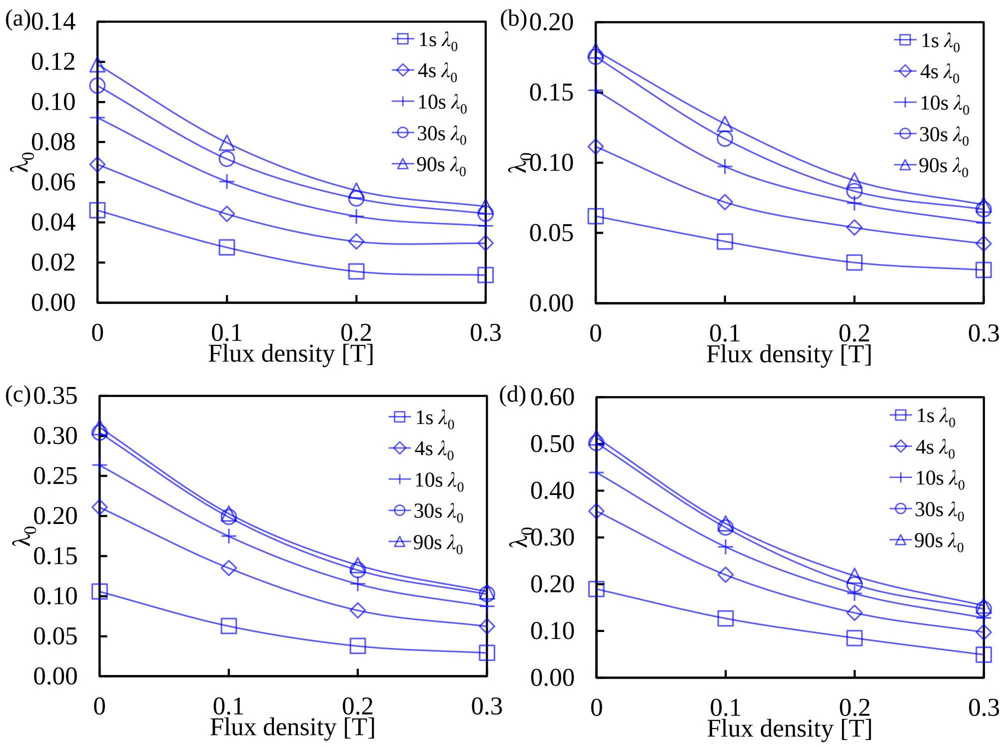


Fig. 9. Influence of magnetic field and resting time on flocculation status of MR gel under shear rates of (a) 3000 s^{-1}. (b) 4000 s^{-1}. (c) 5000 s^{-1}. (d) 6000 s^{-1}.

5. Further discussion on MRG thixotropy

The results in this work indicated the complicated thixotropy in MRG as a result of the coupling of shear flow and magnetic field. Although MRG significantly improves the sedimentation performance and yield stress compared with conventional MR fluid, its thixotropy nature may raise challenges in the practical applications. MR materials in the developed devices, i.e., dampers and clutches, are majorly operate in two modes: shear mode and flow mode. And both operating modes can induce the thixotropy.

For device operating in shear mode, a typical application is MR fluid clutch. The shafts disks and the outer cylinder forms the channel to contain MR fluids. By adjusting the magnetic field that is perpendicular to the shaft disk, the damping property of MR fluid can be tuned, and the different torque transmissibility can be achieved. This operating mode is identical to the twin gap measurement step up in this work. During the clutch running, thixotropy may be involved after the change of speed and altering the magnetic field. If the shaft rotation speed is suddenly increased, the thixotropic yield stress is expected and will gradually decrease to a lower dynamic yield stress. The involvement of the thixotropic yield stress will cause sudden stuck for the clutch during transitions between different speeds. Also, after certain time of shutting off, the increased flocculation state causes a higher thixotropic yield stress. These phenomena are also possible for flow mode device, i.e., MR dampers. In a damper, the piston structures form narrow flow channels with the outer damper cylinder. The piston or the outer cylinder is normally integrated with winding coils that controls the magnetic field in the channel. As the liner motion of the piston takes place, MR fluid flow to the other end of the damper through the channel. In this way, adaptive damping performance can be realized. However, the change of excitation and shutting off lead to different flocculation states thus affect the performance of the damper.

The controlling system may provide solution to compensate or cancel out the thixotropic yield stress. Normally, the rheological models, i.e., Bingham and power law models, only estimate the shear stress response under steady state. The higher values of thixotropic yield stress can be compensated or canceled out by feeding smaller current to the coil then gradually raise the current, as weaker magnetic field exhibits smaller thixotropic yield stress. By introducing the proposed thixotropic model in the control algorithm can provide estimations of the initial flocculation state and the evolution between the thixotropic yield stress steady state stress. Thus, a compensated controlling current can be applied to maintain a smoothed stress response of the adaptive devices.

6. Conclusion

In this work, MRG with 60% weight fraction of CIP was fabricated. Steady shear and stepwise tests were performed to characterise its rheological and thixotropic behaviours. Through the proposed stepwise tests, thixotropy of MRG were revealed and are summarised as follows.

- Higher shear rates contributed to more apparent thixotropy behaviours under all levels of magnetic fields considered.
- Resting resulted in the formation of flocculation in the MRG. The MRG can recover over half of its reversable microstructures within 10s however, longer resting time under magnetic fields could result in irreversible changes due to the formation of large flocs by the magnetized CIPs (remanence occurred).
- The patterns of shear stress decrease (de-flocculation process) under constant shear rate appear to be similar under all magnetic fields. Thixotropic yield stress rapidly approaches to zero after 10-second shearing.
- Magnetic fields induced approx. doubled thixotropic yield stress for MRG. However, the flocculation state λ_0 showed a decreasing trend with the increase of magnetic field.

A phenomenological model was proposed and validated by the experimental data. The model can well describe the thixotropic behaviours mentioned above under all shear rates, resting time and magnetic fields considered. Finally, the discussions on the effects and potential solutions of thixotropy from the engineering application perspective were presented.

Reference

[1] T. Mitsumata, N. Abe, Giant and reversible magnetorheology of carrageenan/iron oxide magnetic gels, Smart materials and structures 20(12) (2011) 124003.

[2] H. Pang, L. Pei, J. Xu, S. Cao, Y. Wang, X. Gong, Magnetically tunable adhesion of composite pads with magnetorheological polymer gel cores, Composites Science and Technology 192 (2020) 108115.

[3] S. Qi, J. Fu, Y. Xie, Y. Li, R. Gan, M. Yu, Versatile magnetorheological plastomer with 3D printability, switchable mechanics, shape memory, and self-healing capacity, Composites Science and Technology 183 (2019) 107817.

[4] Y. Qiao, J. Zhang, M. Zhang, L. Liu, P. Zhai, A magnetic field-and frequency-dependent dynamic shear modulus model for isotropic silicone rubber-based magnetorheological elastomers, Composites Science and Technology 204 (2021) 108637.

[5] Y. Wang, L. Ding, C. Zhao, S. Wang, S. Xuan, H. Jiang, X. Gong, A novel magnetorheological shear-stiffening elastomer with self-healing ability, Composites Science and Technology 168 (2018) 303-311.

[6] J. Zhang, H. Pang, Y. Wang, X. Gong, The magneto-mechanical properties of off-axis anisotropic magnetorheological elastomers, Composites Science and Technology 191 (2020) 108079.

[7] M. Ashtiani, S.H. Hashemabadi, A. Ghaffari, A review on the magnetorheological fluid preparation and stabilization, Journal of Magnetism and Magnetic Materials 374 (2015) 716-730.

[8] S. Li, Y. Liang, Y. Li, J. Li, Y. Zhou, Investigation of dynamic properties of isotropic and anisotropic magnetorheological elastomers with a hybrid magnet shear test rig, Smart Materials and Structures 29(11) (2020) 114001.

[9] Y. Xu, X. Gong, S. Xuan, Soft magnetorheological polymer gels with controllable rheological properties, Smart Materials and Structures 22(7) (2013) 075029.

[10] M. Yu, B. Ju, J. Fu, S. Liu, S.-B. Choi, Magnetoresistance Characteristics of Magnetorheological Gel under a Magnetic Field, Industrial & Engineering Chemistry Research 53(12) (2014) 4704-4710.

[11] J. Mewis, N.J. Wagner, Thixotropy, Advances in Colloid and Interface Science 147 (2009) 214-227.

[12] N. Roussel, Steady and transient flow behaviour of fresh cement pastes, Cement and concrete research 35(9) (2005) 1656-1664.

[13] P. Billberg, Development of SCC static yield stress at rest and its effect on thelateral form pressure, SCC 2005, combining the second North American conference on the design and use of self-consolidating concrete and the fourth international RILEM symposium on self-compacting concrete (2005) 583-589.

[14] Y. Wang, W. Xie, D. Wu, Rheological properties of magnetorheological suspensions stabilized with nanocelluloses, Carbohydrate Polymers 231 (2020) 115776.

[15] Z. Li, D. Li, Y. Chen, H. Cui, Study of the thixotropic behaviors of ferrofluids, Soft Matter 14(19) (2018) 3858-3869.

[16] P. Coussot, Rheometry of pastes, suspensions, and granular materials: applications in industry and environment, John Wiley & Sons 2005.

[17] A. Berker, W. Van Arsdale, Phenomenological models of viscoplastic, thixotropic, and granular materials, Rheologica acta 31(2) (1992) 119-138.

[18] A. Potanin, R. De Rooij, D. Van den Ende, J. Mellema, Microrheological modeling of weakly aggregated dispersions, The Journal of chemical physics 102(14) (1995) 5845-5853.

[19] P. Coussot, J. Raynaud, F. Bertrand, P. Moucheront, J. Guilbaud, H. Huynh, S. Jarny, D. Lesueur, Coexistence of liquid and solid phases in flowing soft-glassy materials, Physical review letters 88(21) (2002) 218301.

[20] C.F. Goodeve, A general theory of thixotropy and viscosity, Transactions of the Faraday Society 35 (1939) 342-358.

[21] P. Coussot, Q.D. Nguyen, H. Huynh, D. Bonn, Avalanche behavior in yield stress fluids, Physical review letters 88(17) (2002) 175501.

[22] N. Roussel, R. Le Roy, P. Coussot, Test of a thixotropy model by comparison with local and macroscopic flow properties, J. Non-Newton. Fluid Mech 117 (2004) 85-95.

[23] N. Roussel, A thixotropy model for fresh fluid concretes: Theory, validation and applications, Cement and Concrete Research 36(10) (2006) 1797-1806.

[24] J.E. Wallevik, Rheology of particle suspensions: fresh concrete, mortar and cement paste with various types of lignosulfonates, Fakultet for ingeniørvitenskap og teknologi 2003.

[25] H. Green, R. Weltmann, Analysis of thixotropy of pigment-vehicle suspensions-basic principles of the hysteresis loop, Industrial & Engineering Chemistry Analytical Edition 15(3) (1943) 201-206.

[26] B. Hu, A. Fuchs, S. Huseyin, F. Gordaninejad, C. Evrensel, Supramolecular magnetorheological polymer gels, Journal of applied polymer science 100(3) (2006) 2464-2479.

[27] S. Li, T. Tian, H. Wang, Y. Li, J. Li, Y. Zhou, J. Wu, Development of a four-parameter phenomenological model for the nonlinear viscoelastic behaviour of magnetorheological gels, Materials & Design 194 (2020) 108935.